Phonon propagation in programmable assemblies of nanoparticles

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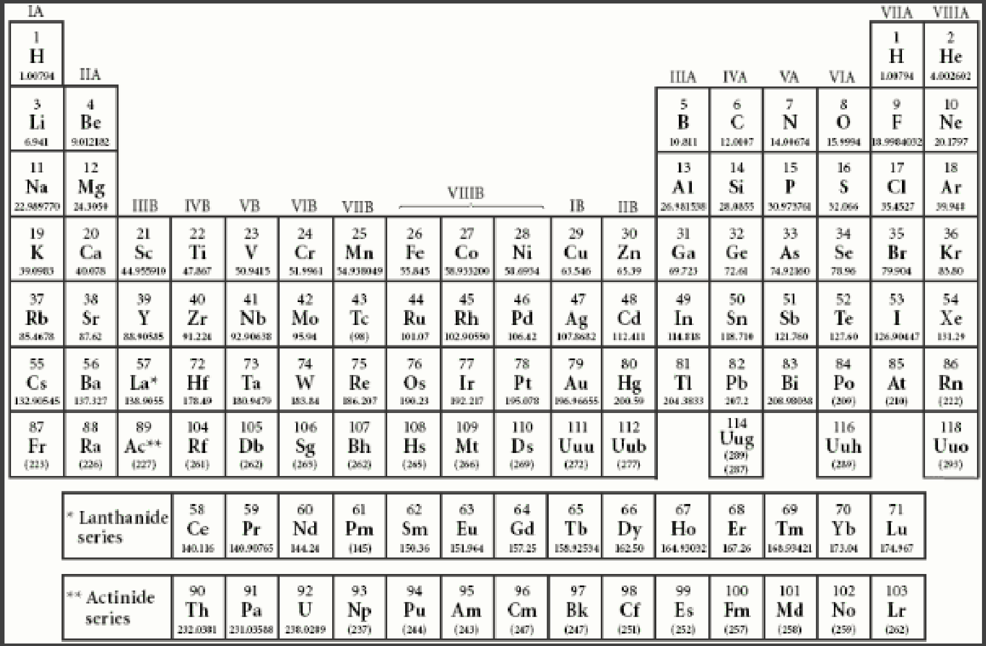
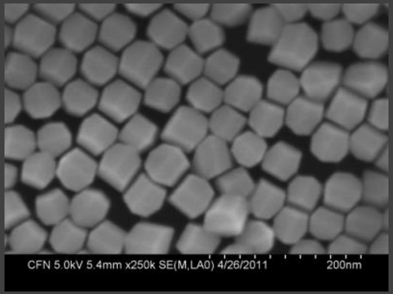
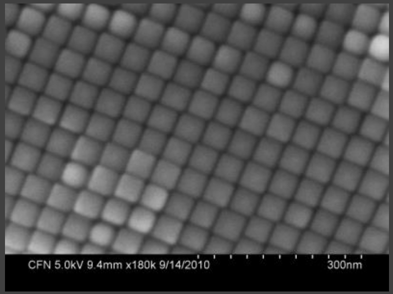
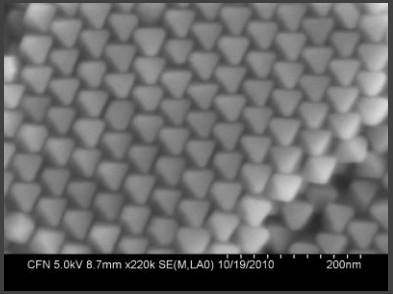
Nanoscale objects



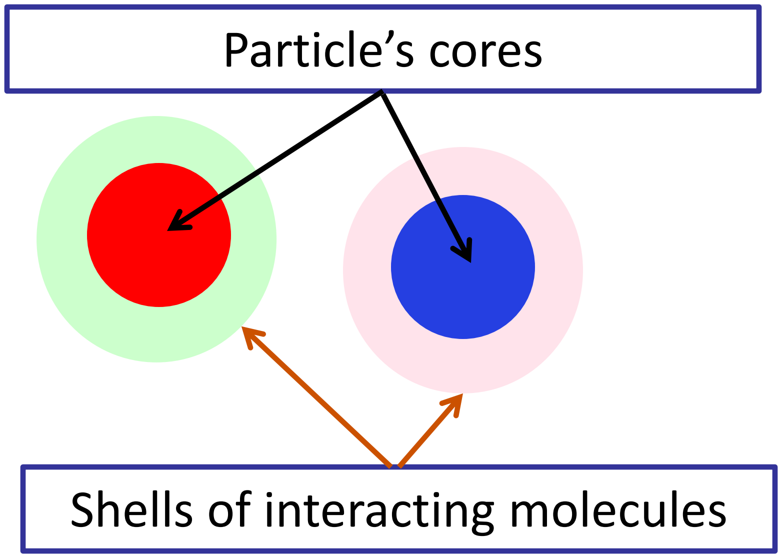
Novel Properties:
- Optical
- Electronic
- Magnetic
- Catalytic

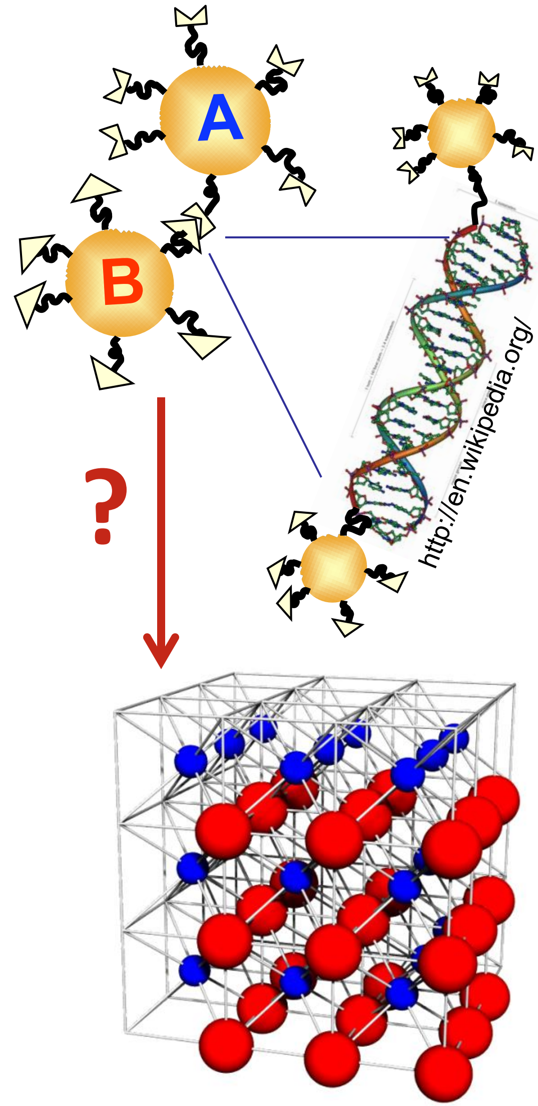




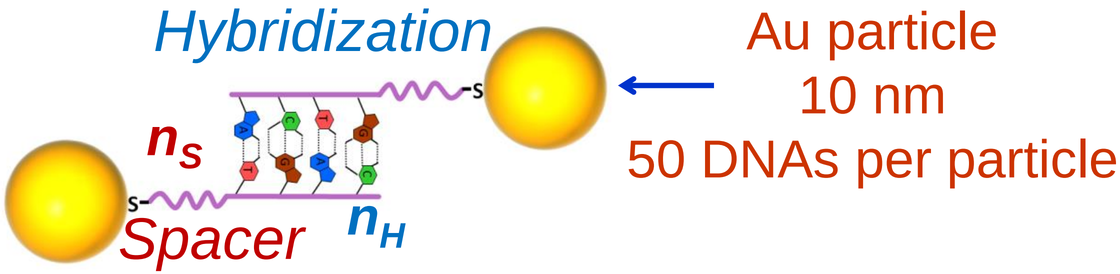


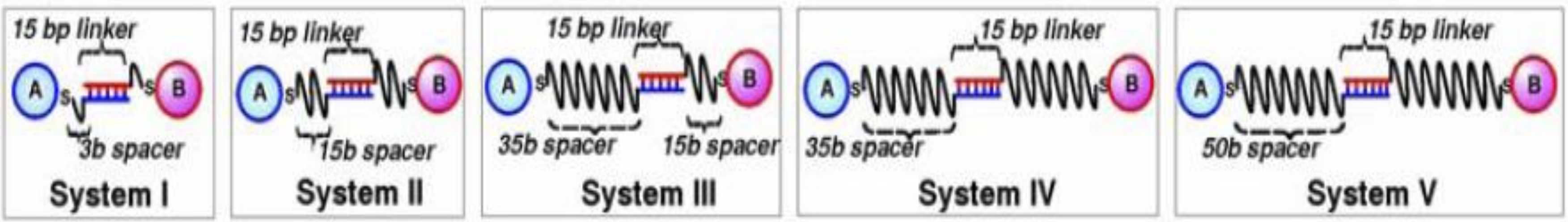
Assembly of Multi-Component Systems



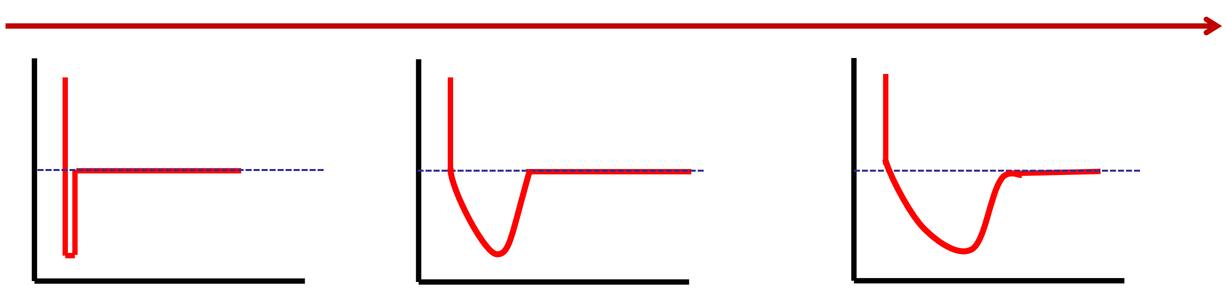


DNA-guided 3D Ordering of Nanoparticles



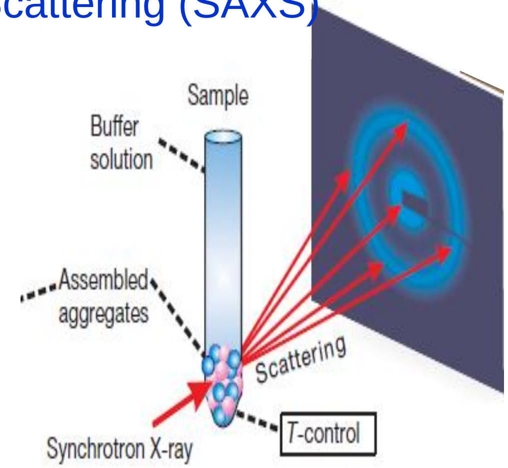


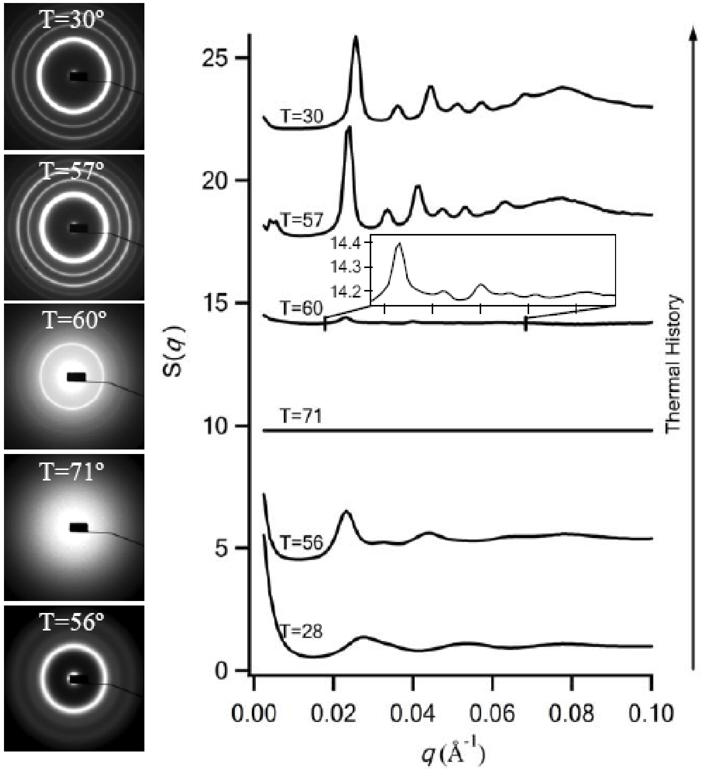
Softness of repulsion

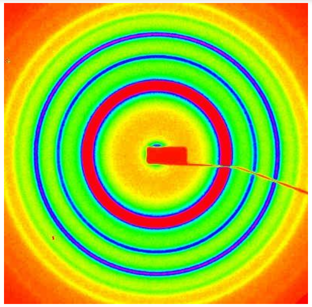


DNA-guided 3D Ordering of Nanoparticles

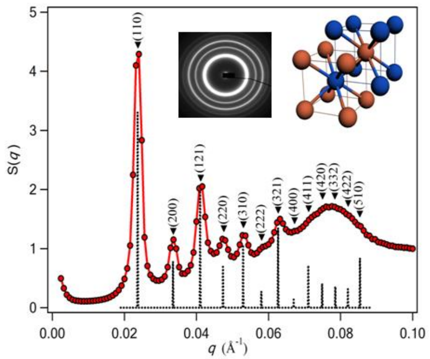
Small Angle X-ray Scattering (SAXS)

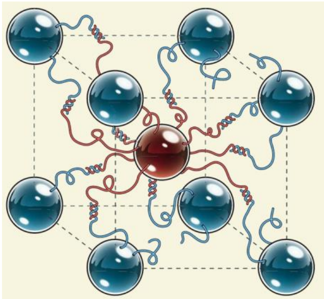






Structure factor





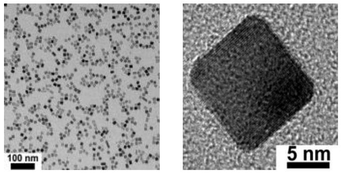
body centered cubic (BCC)

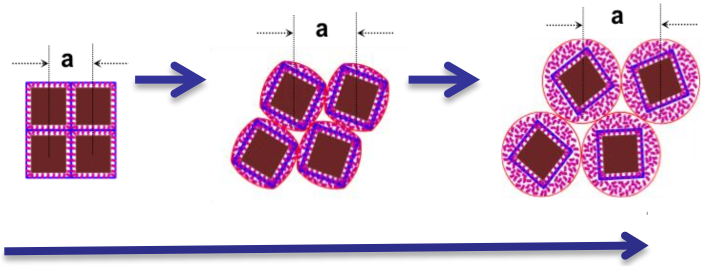
- BCC structure, interparticle distances- tens nm, correlation lengths ~ micron
- Remarkably open structure: nanoparticles and DNA occupy ~3-4% and 6-8% volume

D. Nykypanchuk, M. Maye, D. Van der Lelie, and O. Gang, Nature, 451, 549 (2008)

Shape-induced system transformation

10 nm Pd cube





Ligand (dodecanthiol) layer adsorption via solvent evaporation

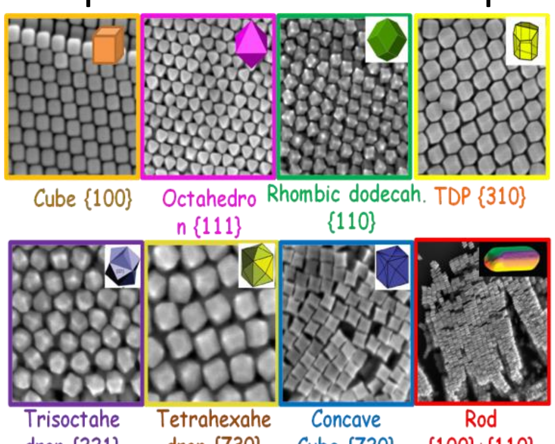
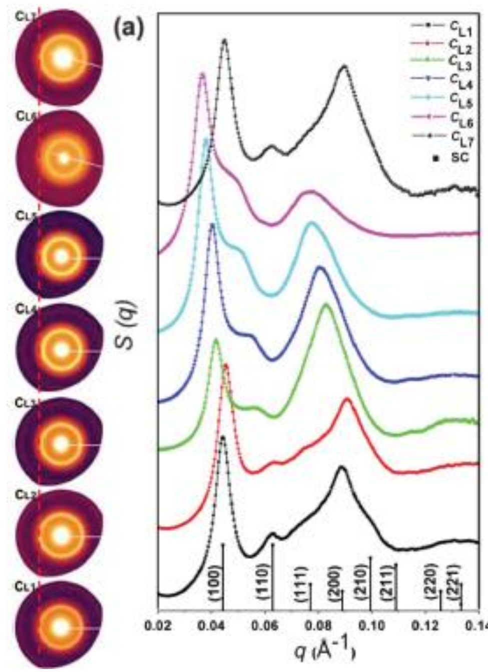


Fig 3:ure. Preliminary results on fabrication of shaped particles (Au) with low- and high- index surfaces using specific adsorbents.



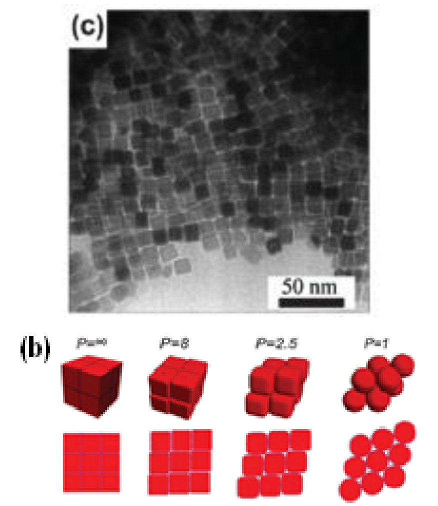


Figure: a) Evolution of the 2D SAXS pattern and the S(Q) of assembled nanocubes at different ligand concentrations. b) 3D scheme of the underlying shape variation; c) TEM image of the nanocubes assembly.

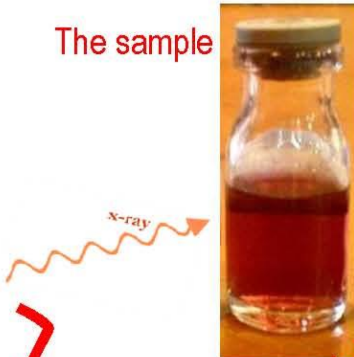
Y. Zhang, F. Lu, D van der Lelie, and O. Gang, Phys. Rev. Lett. 107, 135701 (2011)

Y. Jiao, F. H. Stillinger, S. Torquato, Phys. Rev. E 79. 041309 (2009)

Why IXS?

The outcome of experiments: what can **we learn** from phonon propagation in programmable nanoparticle assemblies?

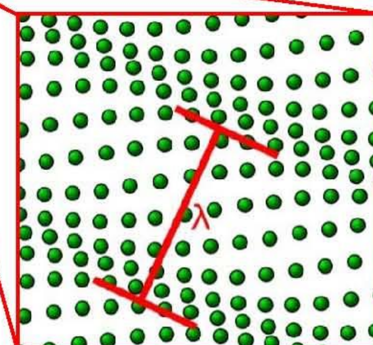
The sample



- Inter-particle phonons: insight on the (tunable) strength of particle linkage
- How phonons are linked to the particle shape and the size? A completely unexplored field….
- How does the damping of phonon relates to macroscopic viscosity of the system? The importance of parallel rheology measurements

Intermediate scale

Probing inter-particle phonons

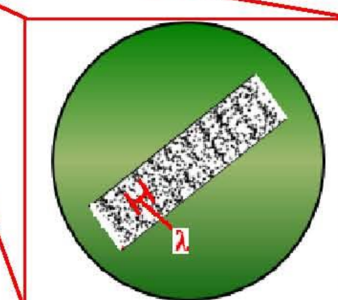


Increasing Q values

- The physics of nm-sized elements is very peculiar and still full of mysteries (different thermodynamics, size-driven metal-to insulator transition, etc….)
- How do intra-particle phonons depend on the particle shape and size? Are they coupled with normal vibrational mode at the particle interface?
- At the highest Qs (ballistic regime) the single particle velocity can be probed, providing insight on the local microscopic viscosity.

Smaller scales

Probing intra-particle phonons



……….towards the development of THz phonic crystals………

What is a phonic crystal?

The intriguing acoustic properties of Eusebio Sempere's sculpture
Madrid, Spain

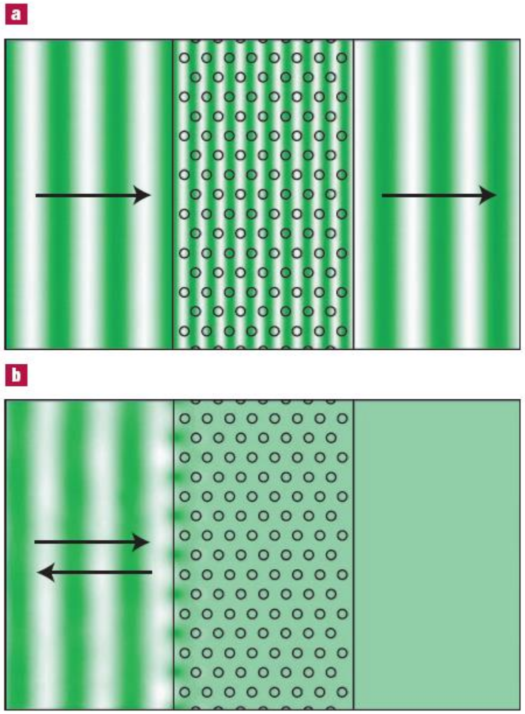
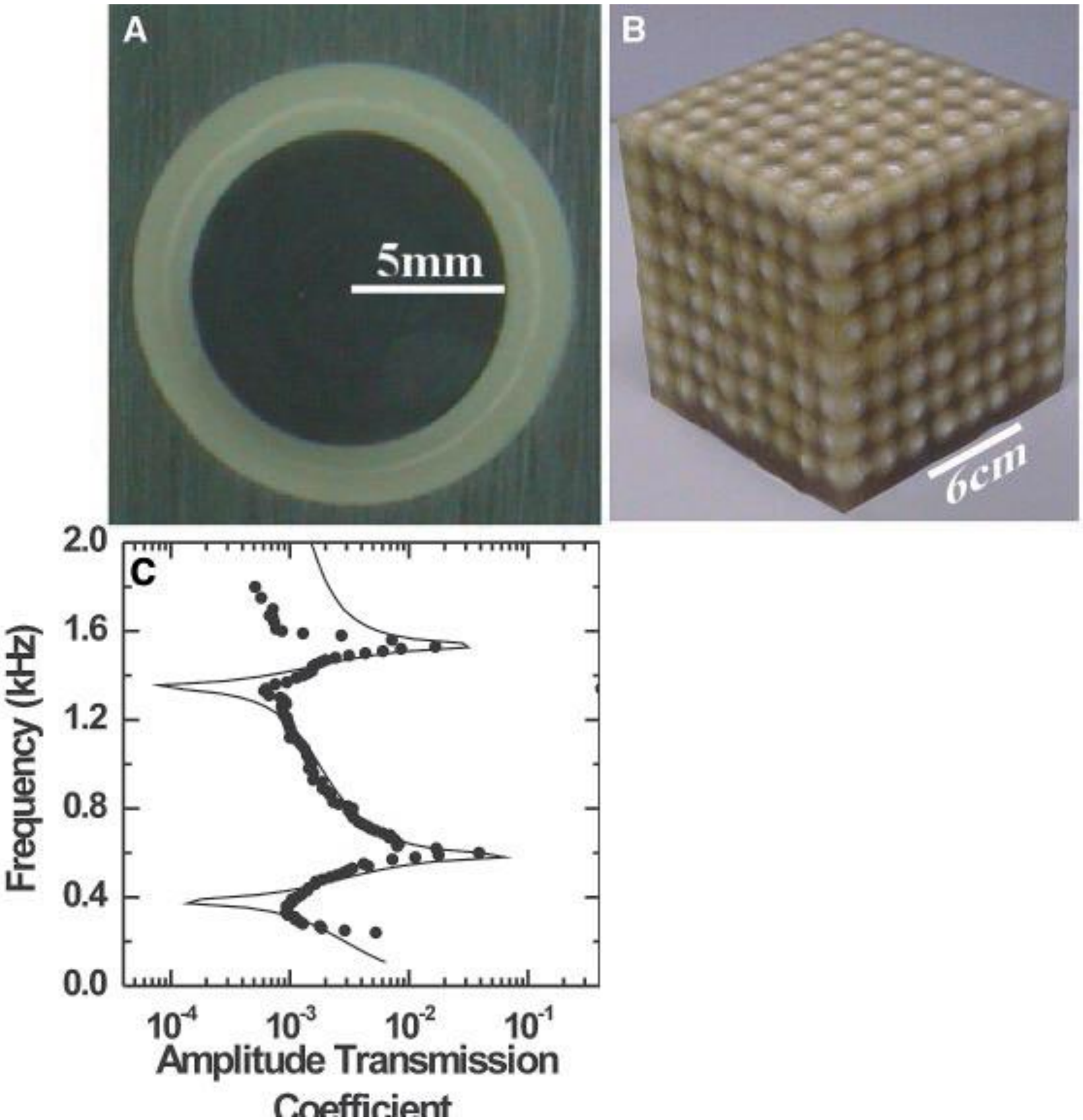


Figure 1 Phononic bandgaps. **a**, A sound wave is incident on the surface of a two-dimensional phononic crystal made of cylinders arranged in a triangular lattice. As the frequency of the incoming wave is not inside the phononic bandgap, the wave is transmitted through the structure. **b**, The sound wave now has a frequency within the gap. The propagation of the wave is not permitted within the phononic crystal and is reflected backwards.

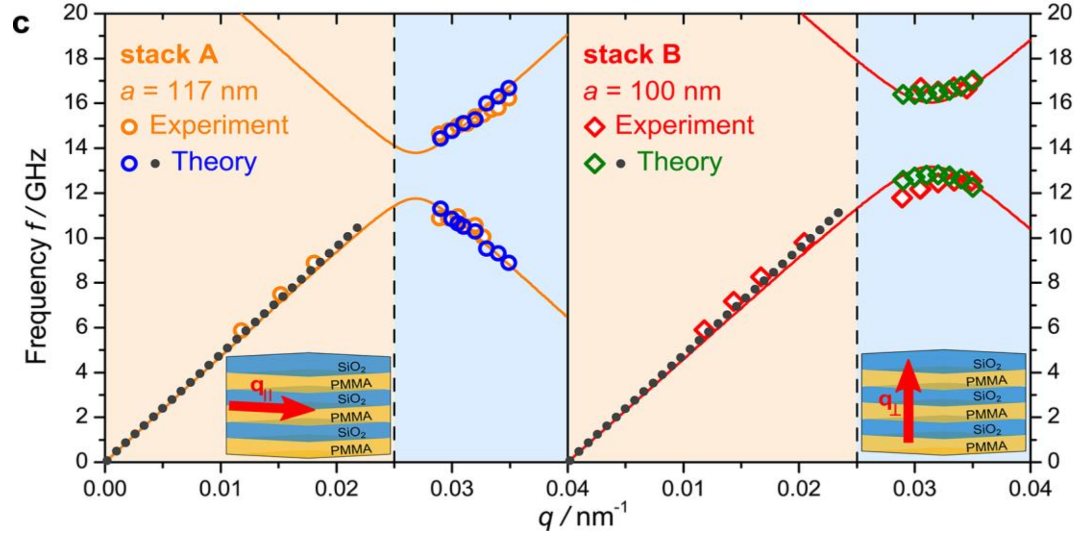
R. Martinez-Sala, et al Nature (London) 378, 241 (1995)

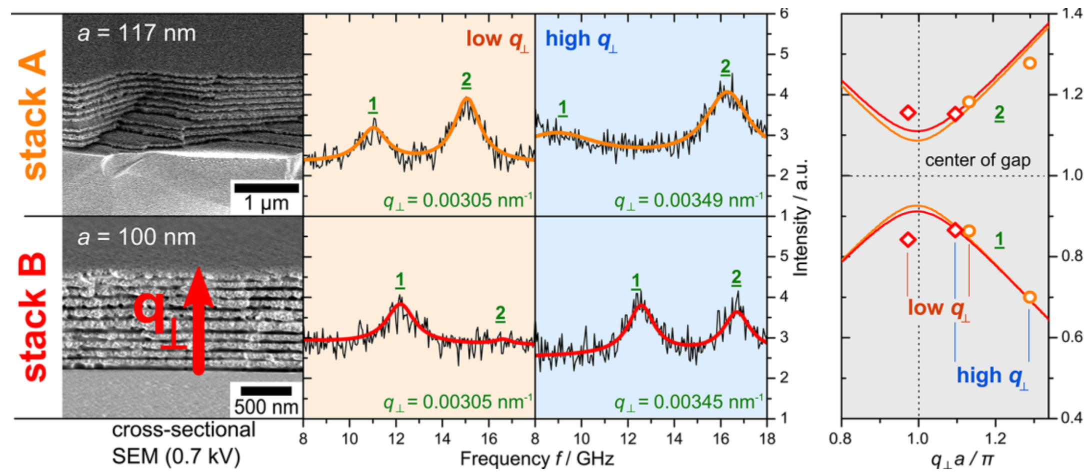
A “sonic frequencies” crystal structure



D. Schneider et al. Nano Lett. **12**, 3101 (2012)

An example of a GHz phononic structure: a stack of PMMA and p-SiO_2

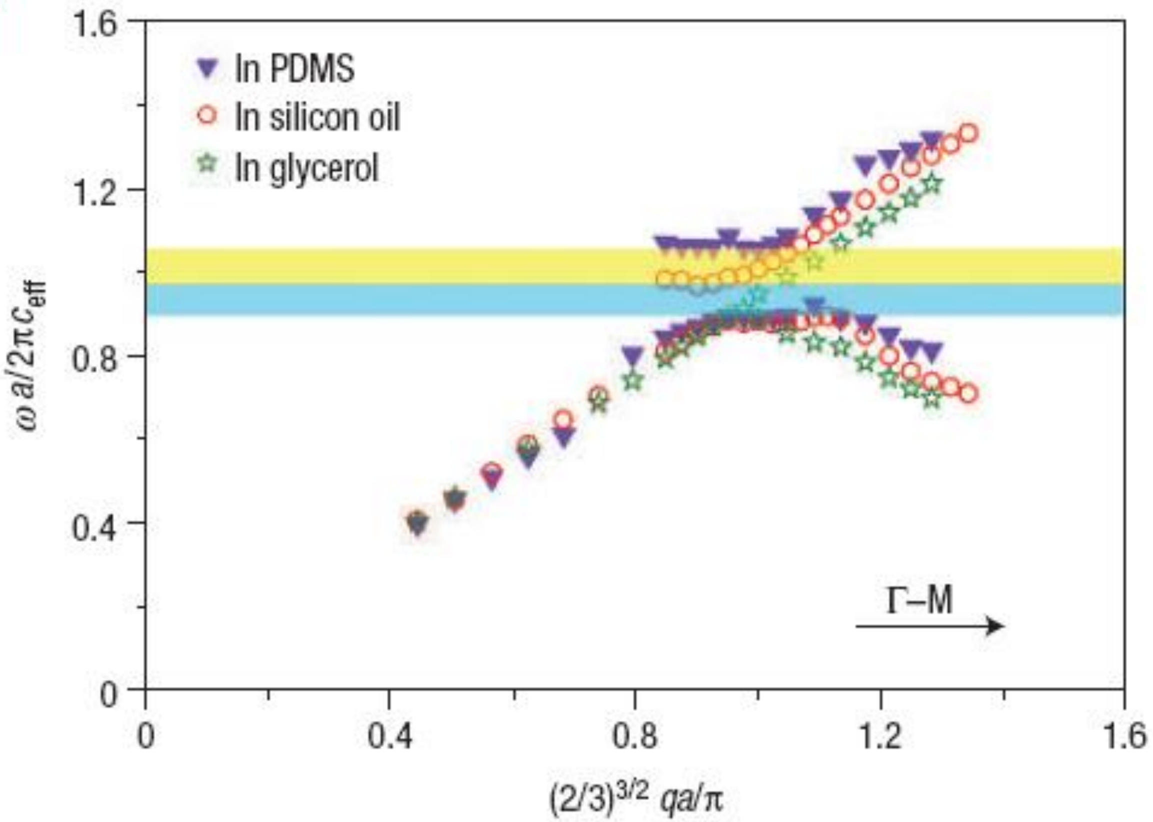




The frequency of the gap scales with the lattice parameter

$$Q_G \approx \left(\frac{3}{2}\right)^{3/2} \frac{\pi}{a}$$

$$\omega_G \approx \frac{2\pi\, c_{eff}}{a}$$



The unique performance of the forthcoming IXS NSLS II spectrometer

Performance needed	Why it is needed	The IXS NSLS II spectrometer
High contrast	Required to cope with the intense quasi-elastic tails of the scattering from particle interface.	The spectrometer will provide an unprecedented essentially Gaussian, spectral contrast.
Access to low and high Qs	Required to probe both the extreme dynamic regime inter-particle phonons the ballistic region.	The new instrument will extend to the low Q value the range probed by current IXS instruments.
Small beam size	Required to study samples inhomogeneous and/or available in small quantity.	The extremely small focal spot the IXS-NSLS II spectrometer is ideal for the purpose.
Low incident energy	The short X Ray photo-absorption length will match the typically small sample thickness, thus maximizing the signal-to-absorption ratio.	The instrument will be the IXS spectrometer operated at the lowest incident energy (9.13 KeV)
High resolution	The high resolution is required at low Q especially for samples having a low sound velocity	The resolution width (1 meV) is only slightly better the current IXS one, however in the mature configuration will be improved by a factor 10.

First day experiment

- Our initial studies will focus on Cubic Pd NPs prepared with a range of sizes, but using low-ligand concentrations in order to limit as much as possible the ligand-to-NP scattered intensity ratio and to shorten the center-to-center inter-NP distance thus moving both the range of inter-particle phonons and the position of the phononic gap to more accessible (higher) Q values.

- The cubic shape was chosen because it represents the only platonic (regular) solid uniformly filling 3D-space, thus limiting the voids occupied by the ligand and allowing a closer packing of NP units.

- The choice of Pd as a material is also suggested by existing SAXS characterization of Pd assemblies, where an intriguing shape evolution upon ligand evaporation was demonstrated.

- However, Ag NPs will also be considered as a material since the sound velocity of Ag is 20% higher than for Pd and this is expected to move the dynamic gap to higher energies.

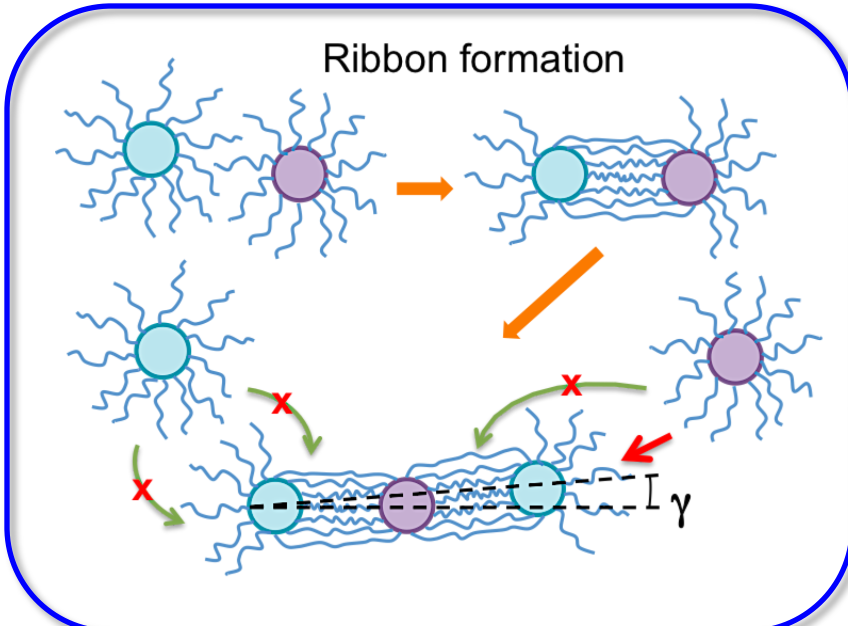
Conclusion

- The study of programmable assemblies of nanoparticles will shed a deeper insight onto a very rich and still unexplored phenomenology.

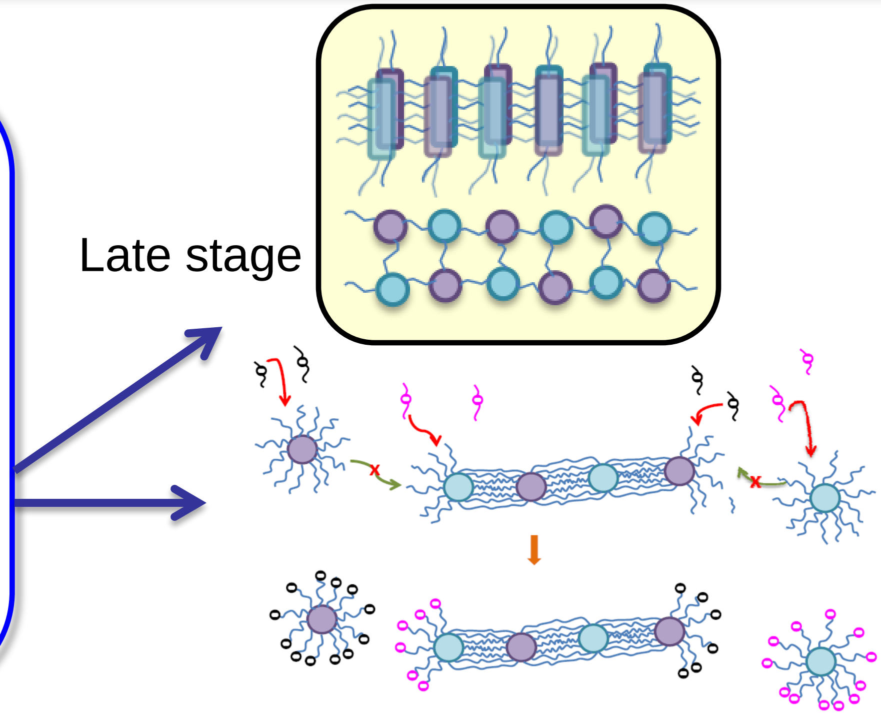
- It will open the way to the exploration of a new science frontier: characterization of the inter- and intra-particle high frequency elastic (acoustic) properties of CFN-synthesized NP superlattice assemblies.

- This may lead to the development of THz phononic structures and high-impact first experiments using the unique capabilities of the NSLS-II Inelastic X-ray Scattering beamline.

Assembly of Rods



Side view of rods

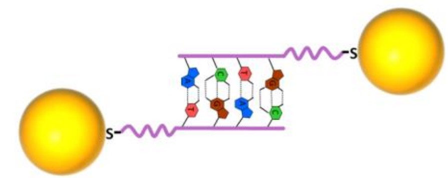


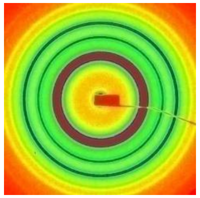
Arrested state, using molecular blocker

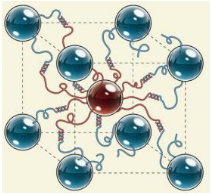
- Spontaneous symmetry break during assembly: flexibility of the chains and their collective effect
- Hierarchical assembly: time separated regimes for intra- and inter-ribbon assembly and the reversibility of DNA binding

Summary

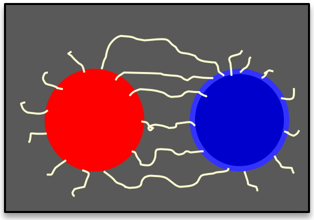
Soft shells with recognition interactions result in 3D order

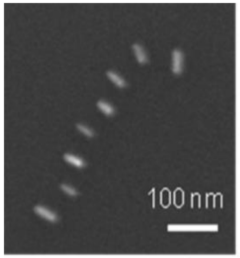




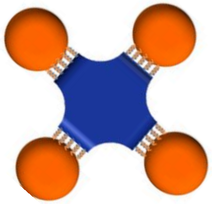


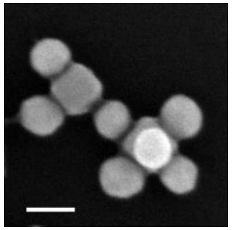
Polymeric effects for radially symmetric shells can lead to anisotropic interactions

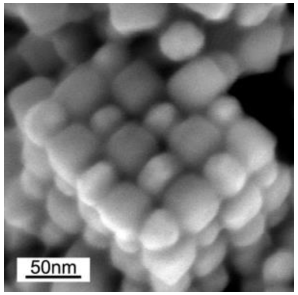




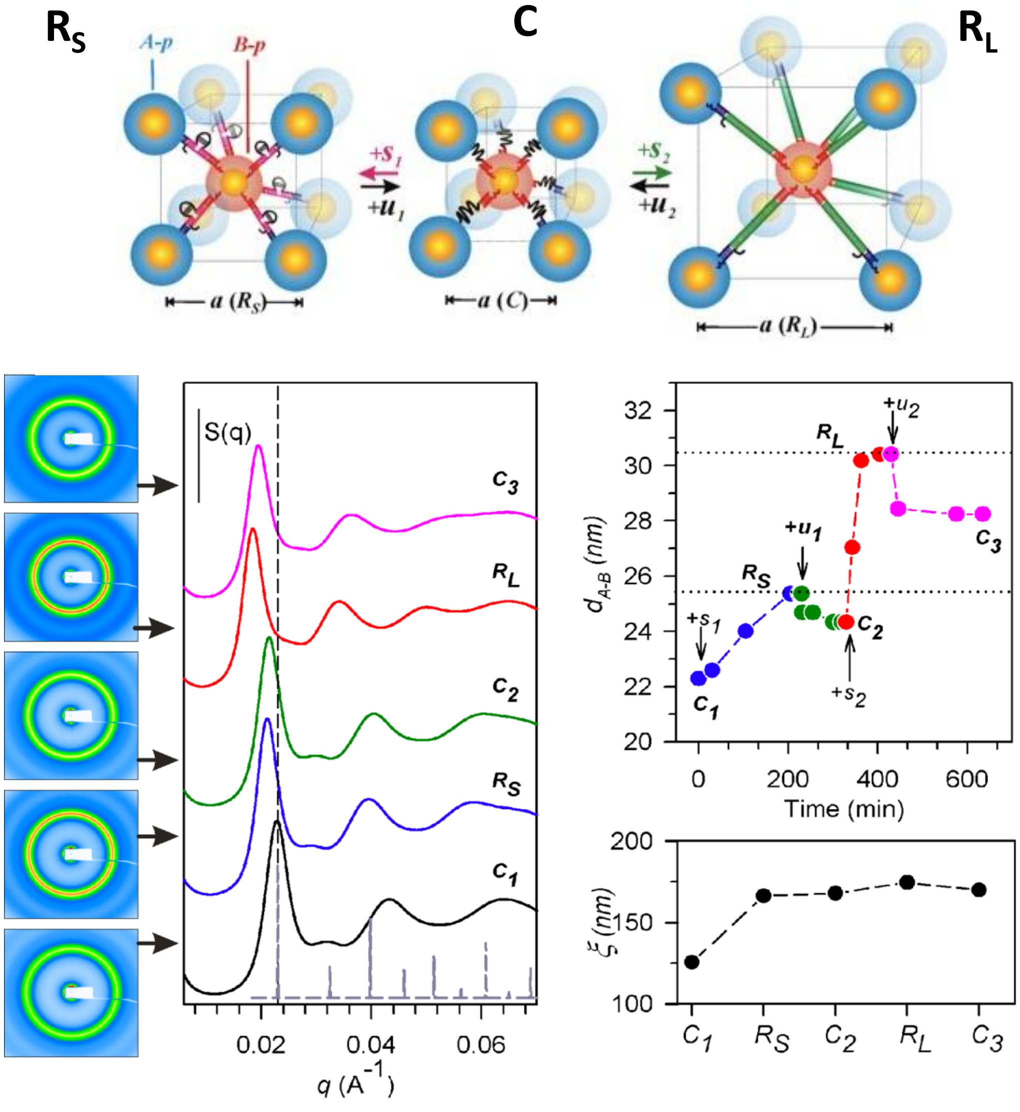
Anisotropic objects determine local order and lattice symmetry







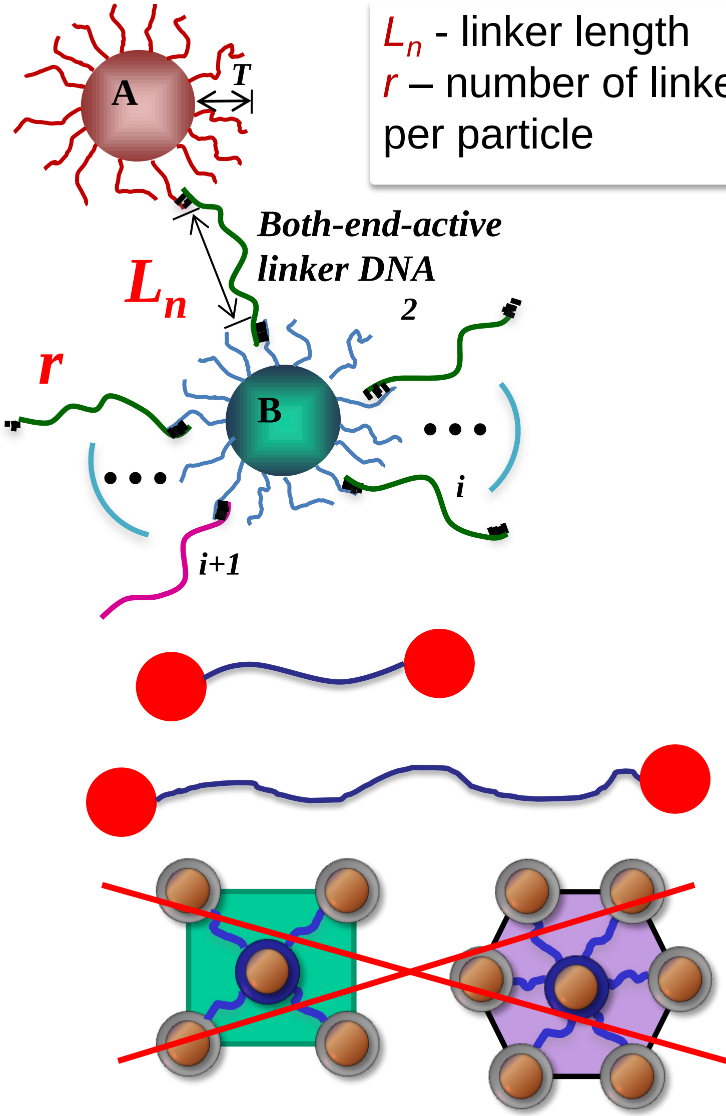
Switchable 3D Superlattices

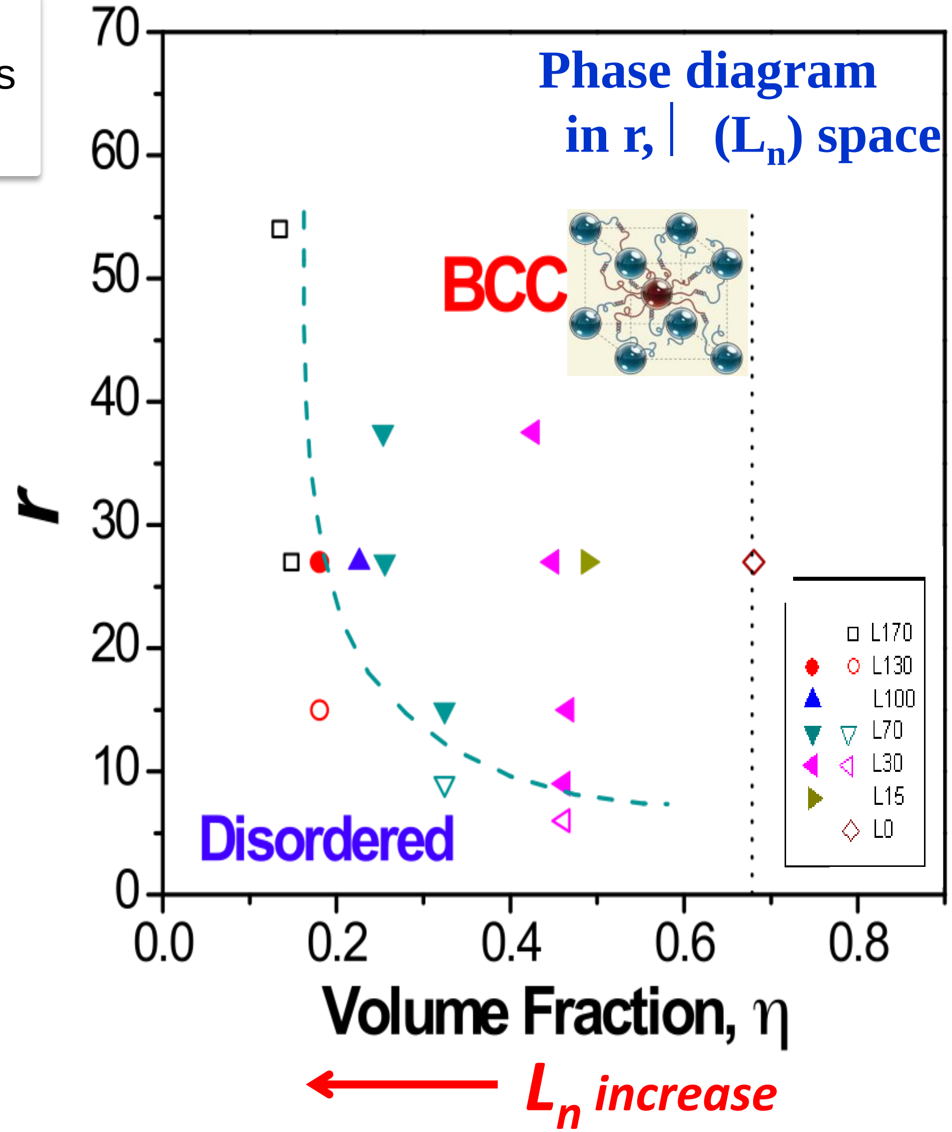


Nature Nanotechnology 6, 116, (2010)

DNA Linker Mediated Assembly

L_n - linker length
r – number of linkers per particle





H. Xiong, D. Van der Lelie, and O. Gang, *Jour. Amer. Chem. Soc., 130 (8), 2442 (2008)*
H. Xiong, D.van der Lelie and O. Gang, Phys. Rev. Lett., 102 *(2009)*

Acknowledgments

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Masa Fukuto
Kevin Yager

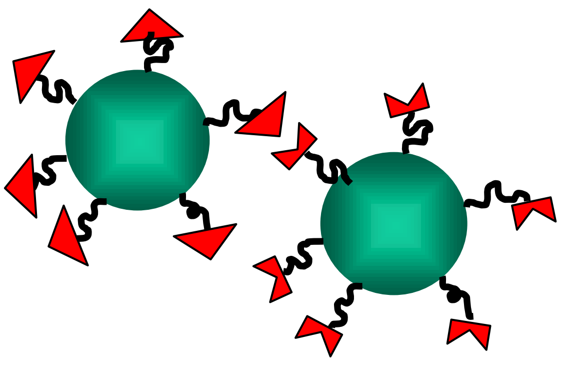
Center for Functional Nanomaterials

NSLS (X9, X21, X6B, X22B)

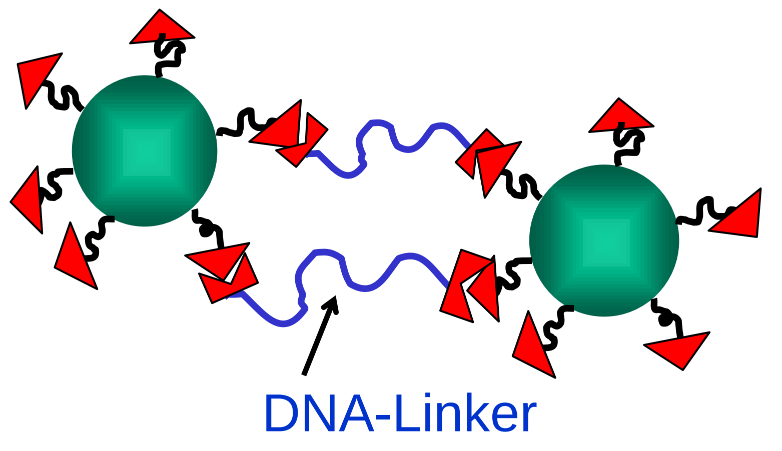
Supported by
US DOE Office of Basic Energy Sciences

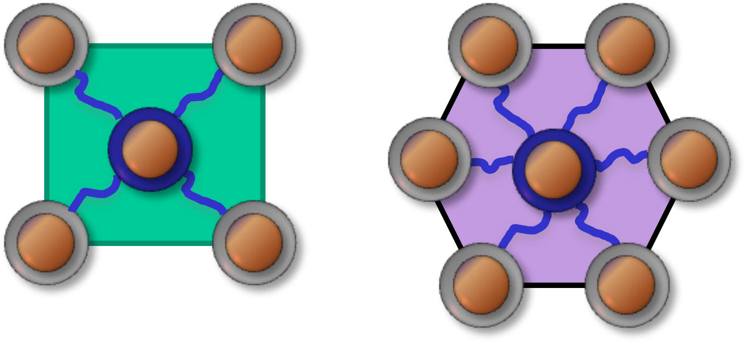
Assembly via Direct Hybridization and DNA-Linkers

Direct particles hybridization

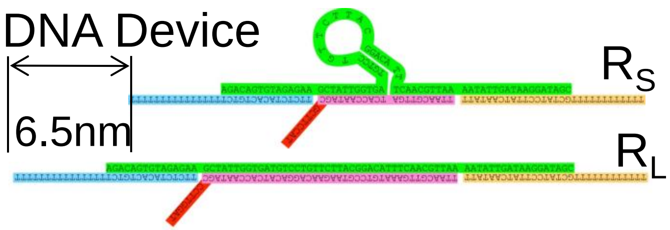


Linker mediated hybridization



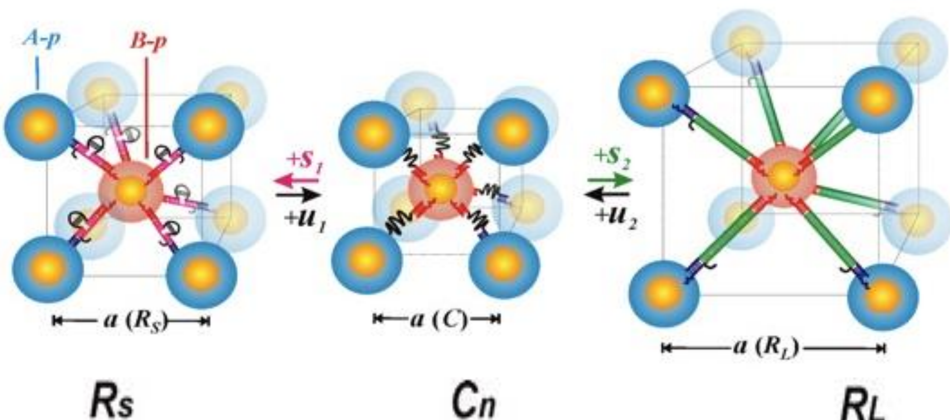


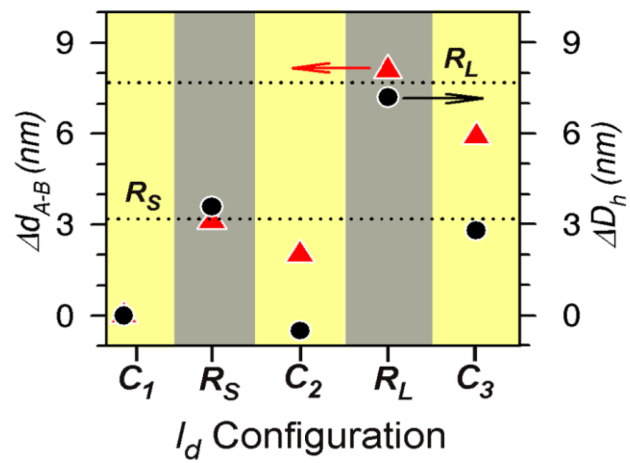
Molecularly switchable nano-systems



Switchable DNA Device

- Switches interparticle distances
- Assembles and manipulates 3D structures





Molecular stimuli s_1

Molecular stimuli s_2

Rigid short (R_s) linker with a loop

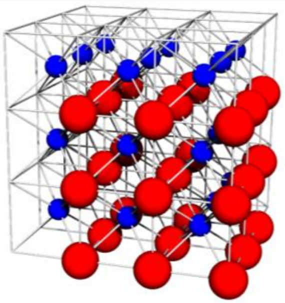
Coiled (C_n) linker

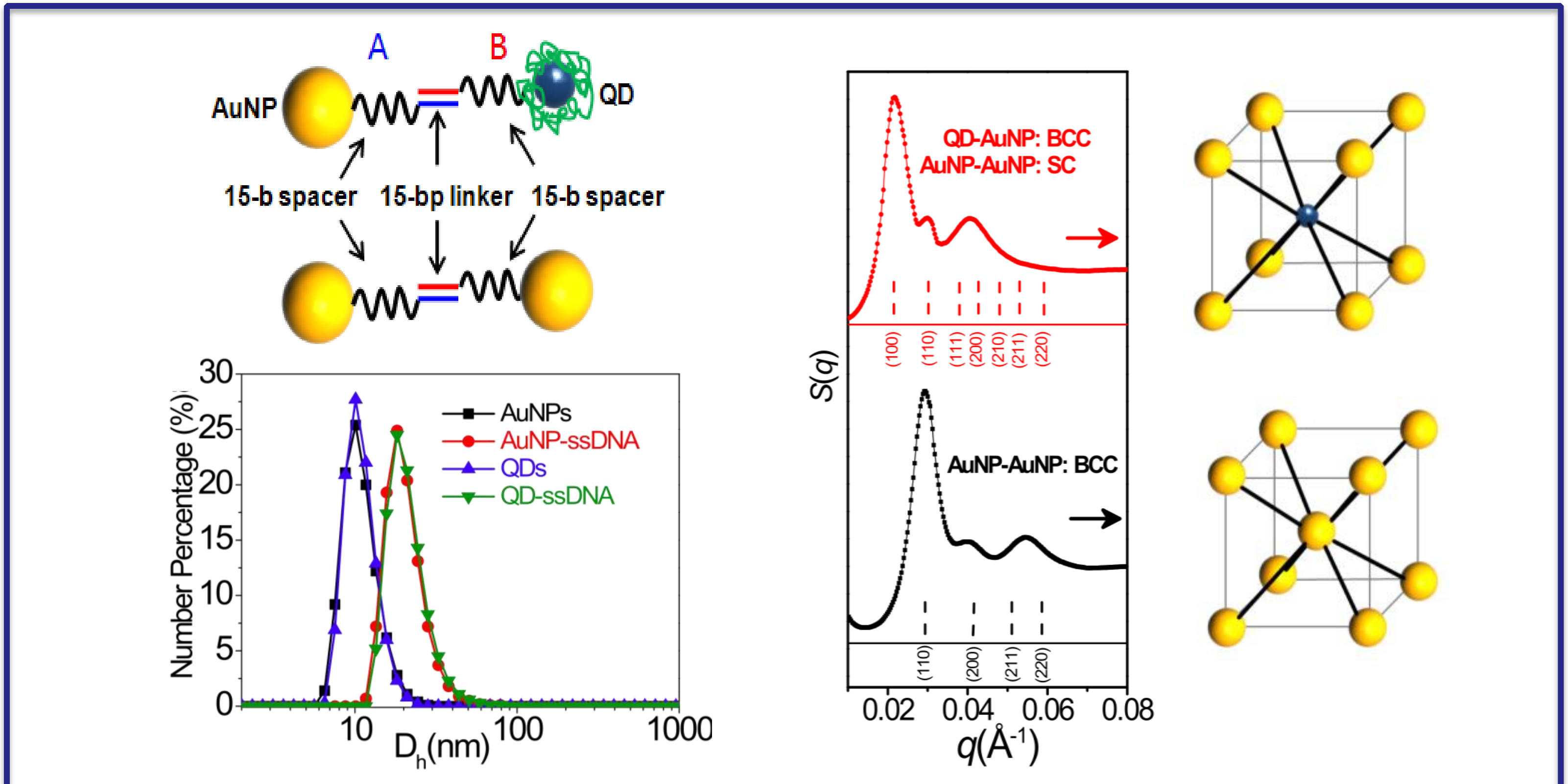
Rigid long (R_L) linker

Nature Nanotechnology 6, 116, (2010)

Binary Superlattices from CdSe and Au particles

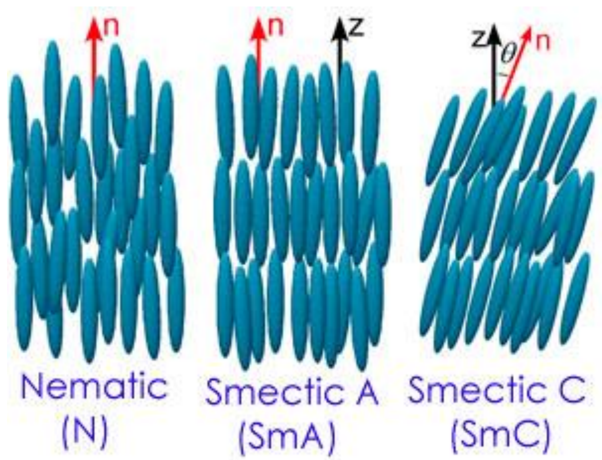
- **Assembly of gold-semiconductor (CdSe, quantum dot, QD) lattice**

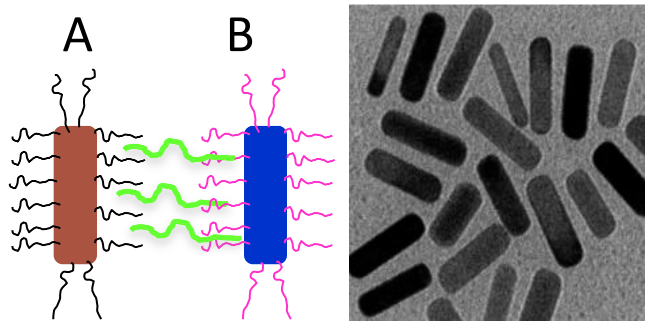




D. Sun and O. Gang, JACS (2011), *33* (14), 5252

Assembly of Rods

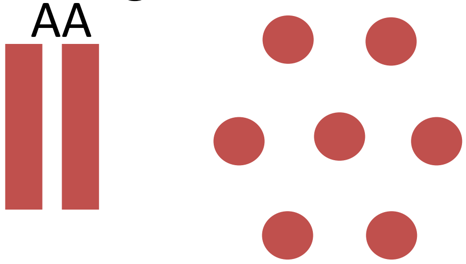




~ 10 nm X 40 nm

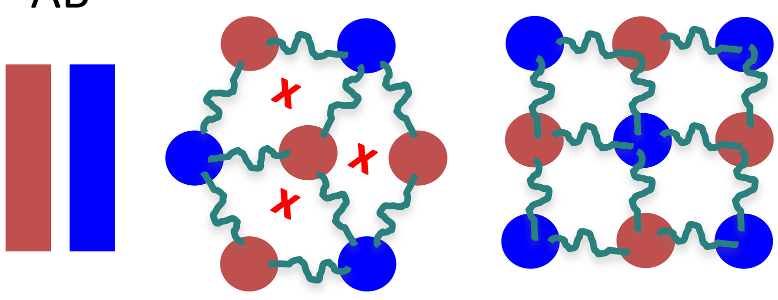
Hexagonal Phase

AA

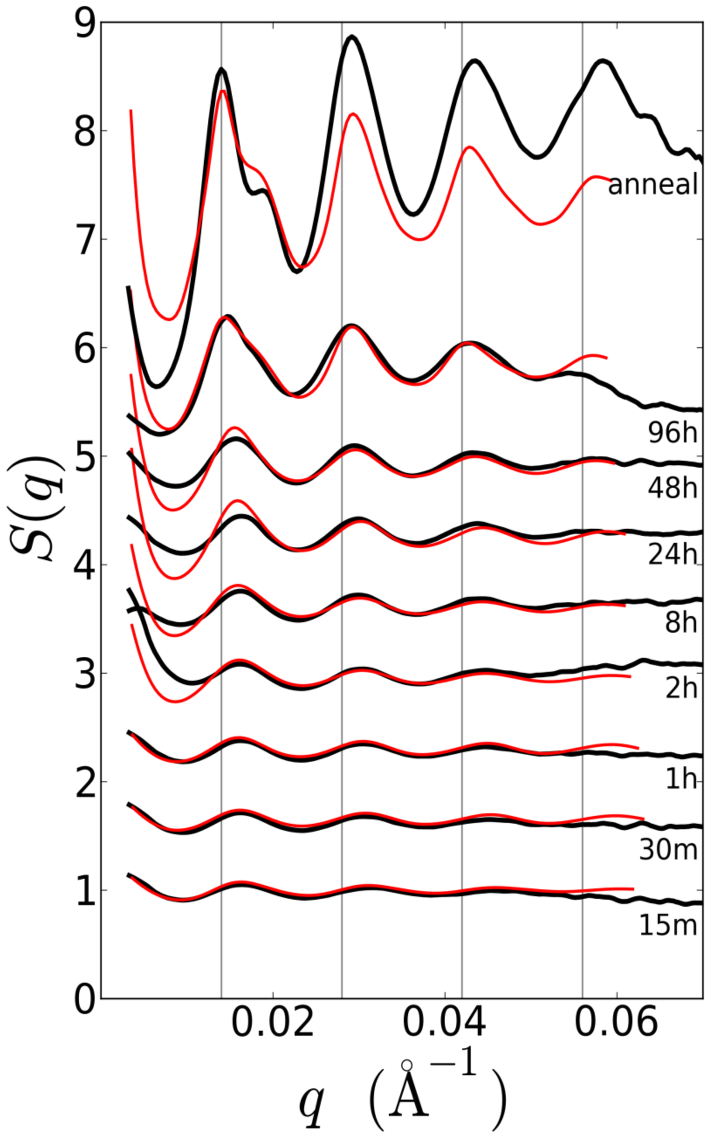


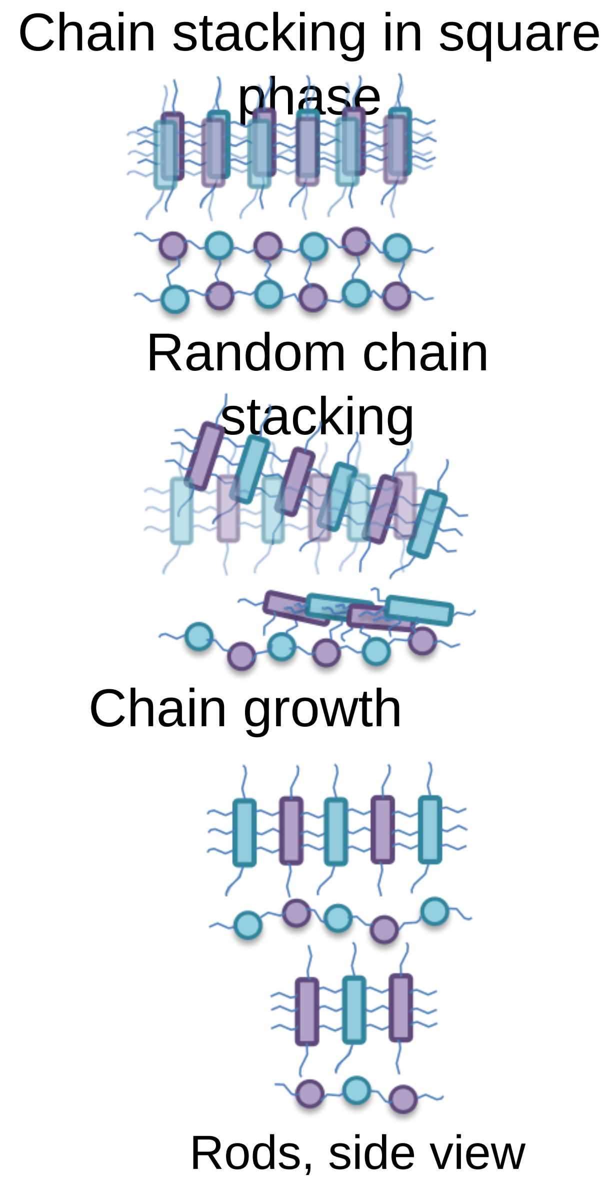
?

AB



Kinetics of Rods Assembly

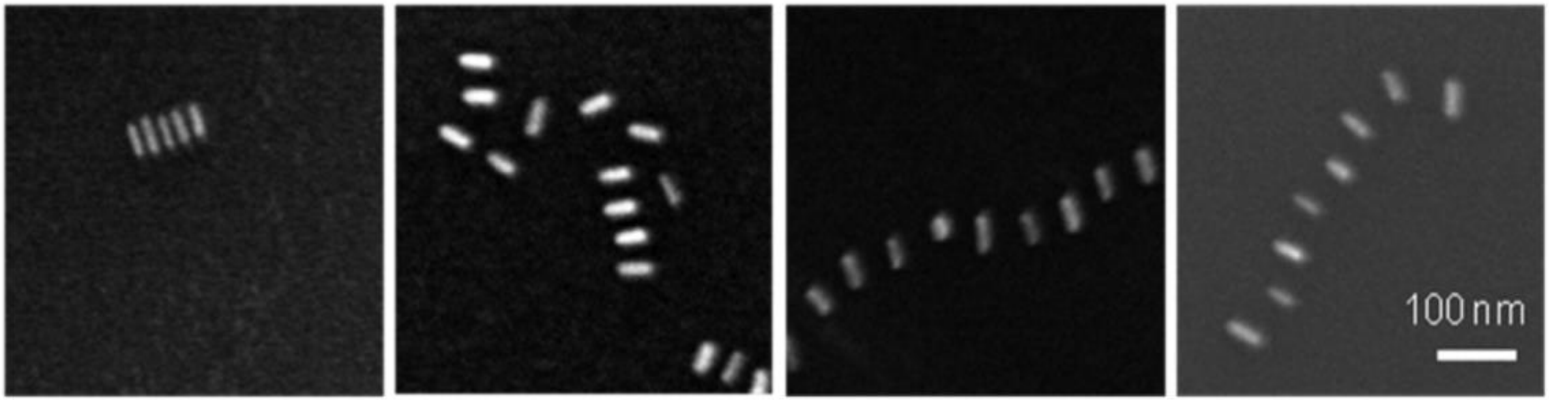




S. Vial et al, ACS Nano 7 (6), 5437, 2013

Assembly of Rods

1D ribbons of parallel rods for different lengths of DNA linkers



DNA length increase

S. Vial et al, ACS Nano 7 (6), 5437, 2013